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REC'D 20 JUL 2001

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PFC 1465 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/02387	International filing date (day/month/year) 20/06/2000	Priority date (day/month/year) 24/06/1999
International Patent Classification (IPC) or national classification and IPC C01B3/40		
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 5 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none">I <input checked="" type="checkbox"/> Basis of the reportII <input type="checkbox"/> PriorityIII <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicabilityIV <input type="checkbox"/> Lack of unity of inventionV <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statementVI <input type="checkbox"/> Certain documents citedVII <input type="checkbox"/> Certain defects in the international applicationVIII <input type="checkbox"/> Certain observations on the international application		
Date of submission of the demand 16/01/2001	Date of completion of this report 18.07.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Mayne, J Telephone No. +49 89 2399 8572 	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02387

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1,4,6,7	as originally filed			
2,3,5	as received on	05/07/2001	with letter of	02/07/2001

Claims, No.:

1-8	as received on	05/07/2001	with letter of	02/07/2001
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Drawings, sheets:

1/2,2/2	as originally filed
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2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02387

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB00/02387

R e a s o n e d S t a t e m e n t

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document: D1 EP-A-0884271

Article 33(2) and (3) PCT

None of the cited prior art documents discloses all the features of the independent claims 1 and 2. Claims 1-8 are therefore novel and fulfill the requirements of Article 33(2) PCT.

D1 is concerned with a methanol reformer which contains a catalyst and is used to supply H₂ to a fuel cell (e.g. claim 1 of D1 and abstract). D1 discusses various ways to reactivate the catalyst whilst it is being used which include:

reducing the fuel load; raising the temperature; increasing the air λ value to increase the O₂ excess

(see col. 3, l. 10-26, claim 1, col. 5, l. 1st paragraph and col. 6, l. 33-36).

For the catalyst to be regenerated the reforming reaction is interrupted according to D1, claim 1. D1 does not specify that fuel, air and steam continue to be passed through a reforming catalyst during the regeneration phase.

In the examples of the application in which fuel, air and steam continue to be passed through a reforming catalyst whilst regeneration occurs, either using air pulses or raised temperature, the Applicant has shown that he can maintain a hydrogen concentration of above 25% throughout the operation (example 2, Fig. 1b, example 3). This effect can also be achieved by increasing the steam feed rate (example 5) or by inhibiting deactivation of the catalyst either using an additive (example 4) or extra air (example 6).

Modulating the fuel feed-rate would also alter the oxygen to carbon ratio and be expected to have a similar effect as modifying the air feed-rate.

Since the methods of claims 1 and 2 are not derivable directly from D1 and the technical effects thereby achieved are not foreseeable from D1 an inventive step is accorded.

Claims 1-8 fulfill the requirements of Article 33(3) PCT.

Because the performance of the reformer has a direct effect on the power output from the fuel cell, deactivation of the catalyst cannot be allowed to proceed unchecked. However the process of power generation cannot be stopped to allow regeneration of the reformer, when its performance falls below an acceptable level. The regeneration of such catalytic reactors whilst they are in use is the problem this invention sets out to solve.

In many instances, the performance of the catalyst declines while it is being used. Although the rate of decline can usually be reduced by changing the operating conditions, it is often accompanied by a drop in hydrogen and power output. One frequently practised method for restoring the performance of a fuel processor is to replace the catalyst periodically. Another method involves regenerating the catalyst while it remains in the processor, using a prescribed regeneration procedure (eg see JR Rostrup-Nielsen in Catalysis Today, Vol 37, 1997, p 225-232). However, both these require that the process of hydrogen-generation is interrupted in order to restore performance.

Thus in a first aspect, the present invention provides a method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

The reforming catalyst may be one component of the catalytic fuel processor, or it may be the only component. Where loss of performance is being caused by a particular component in a complex fuel mixture, the regeneration method can be targeted at the specific deactivating effect.

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Thus in a second aspect, the present invention provides a method for preventing or retarding the de-activation of a catalytic fuel processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

- 10 - continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
 - continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
 - 15 - continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel,
 - continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.
- 20 and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

Again, the reforming catalyst may be one component or the only component of the catalytic fuel processor. In a preferred embodiment of the invention water is temporarily added to the feed. ('Feed' is a term used to describe the reactant mixture supplied to the fuel processor.) The water will be rapidly converted into steam in the catalyst. The water (steam) to carbon ratio in the feed may readily be adjusted in order to permit targeting of the regeneration method to a specific deactivating event. Adjusted for the purposes of this invention means increased or decreased. The oxygen to carbon ratio
30 may also be adjusted for the same purpose, by adding or changing the feed-rate of air, or by changing the feed-rate of the fuel.

Figure 1b shows the effect of air pulses on the composition of dry reformat during reforming of dodecane (as described in Example 2).

In both cases % in reformat is on the vertical axis and time/hours is on the horizontal axis.

- 5 ♦ represents Hydrogen, ■ represents carbon monoxide, and ▲ represents carbon monoxide.

Figure 2a shows the composition of dry reformat as a function of time during the reforming of toluene under the two conditions described in example 5.

- 10 Figure 2b shows the effect of increasing the air feed-rate on the composition of dry reformat, during reforming of toluene (as described in example 6).

In both cases the left hand side of the vertical axis represents % in reformat and the right hand side of the vertical axis represents temperature in °C. The horizontal axis represents time/hours; ♦ represents hydrogen, ■ represents carbon dioxide,

- 15 ▲ represents carbon monoxide and x represents temperature.

It will be appreciated that many variations can be made to the invention herein described without departing from the present inventive concept.

20 **Example 1 (Aliphatic fuel ; no regeneration)**

- A bed (0.2 g) of reforming catalyst was packed into a tubular quartz reactor, which was positioned at the centre of a furnace. A mixture of dodecane vapour (produced by vaporising the liquid at a rate of $4 \text{ cm}^3 \text{ hour}^{-1}$), air ($200 \text{ cm}^3 \text{ min}^{-1}$) and
25 steam (produced by vaporising water at a rate of $4 \text{ cm}^3 \text{ hour}^{-1}$) was passed through the catalyst bed, which was heated by the furnace. The furnace temperature was maintained at 500°C . The product stream (ie the reformat) passed through a drier before entering a gas chromatograph, which was used to analyse for hydrogen. The initial concentration of hydrogen in the dry reformat was just above 25%, but declined to 20% within an
30 hour, and to 15% within 4 hours. See Figure 1a for results.

CLAIMS

1. A method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

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- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and
10 ~~modulating the air and/or steam feed rate,~~
- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

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and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

2. A method for preventing or retarding the de-activation of a catalytic fuel
20 processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

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- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- 30 - continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

3. A method according to either claim 1 or claim 2, whereby water is temporarily
5 added to the fuel.

4. A method according to claims 1 or 2 in which air is temporarily added to the feed.

10 5. A method according to claims 1 or 2 in which an additive is added to the feed.

6. A method according to claim 5 in which the additive is an oxygenate.

7. A method according to claim 6 in which the oxygenate is MTBE
15 (methyl-tert-butylether).

8. A method according to claims 1 or 2 in which the catalyst bed temperature is raised temporarily by an external heat source.

20 9. A method according to claims 1 or 2 in which the temperature of one or more of the reactant feeds is raised temporarily.

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

TO:
WISHART, Ian, Camille
Johnson Matthey Technology Centre
Blounts Court
Sunning Common
Reading RG4 9NH
GRANDE BRETAGNE

by fax and post

Date of mailing
(day/month/year)

18.07.2001

Applicant's or agent's file reference
PFC 1465 PCT

IMPORTANT NOTIFICATION

International application No.
PCT/GB00/02387

International filing date (day/month/year)
20/06/2000

Priority date (day/month/year)
24/06/1999

Applicant

JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



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Form PCT/PEA/416 (July 1992)


0 AUG 2001

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's reference PCT/1465/PCT		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/1PEA/416)																	
International application No. PCT/GB00/02387	International filing date (day/month/year) 20/06/2000	Priority date (day/month/year) 24/06/1999																	
International Patent Classification (IPC) or national classification and IPC C01B3/40																			
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<p>1. This International preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.15 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 5 sheets.</p>																			
<p>3. This report contains indications relating to the following items:</p> <table border="0"> <tr> <td>I</td> <td><input checked="" type="checkbox"/> Basis of the report</td> </tr> <tr> <td>II</td> <td><input type="checkbox"/> Priority</td> </tr> <tr> <td>III</td> <td><input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td>IV</td> <td><input type="checkbox"/> Lack of unity of invention</td> </tr> <tr> <td>V</td> <td><input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td>VI</td> <td><input type="checkbox"/> Certain documents cited</td> </tr> <tr> <td>VII</td> <td><input type="checkbox"/> Certain defects in the International application</td> </tr> <tr> <td>VIII</td> <td><input type="checkbox"/> Certain observations on the international application</td> </tr> </table>				I	<input checked="" type="checkbox"/> Basis of the report	II	<input type="checkbox"/> Priority	III	<input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	IV	<input type="checkbox"/> Lack of unity of invention	V	<input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	VI	<input type="checkbox"/> Certain documents cited	VII	<input type="checkbox"/> Certain defects in the International application	VIII	<input type="checkbox"/> Certain observations on the international application
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Date of submission of the demand 18.07.2001		Date of completion of this report 18.07.2001																	
Name and mailing address of the International preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399-0 Tx: 823656 epmu d Fax: +49 89 2399-4485		Authorized officer Mayne, J Telephone No. +49 89 2399 8572																	



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**International application No. **PCT/GB00/02387****I. Basis of the report**

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):*

Description, pages:

1, 4, 6, 7	as originally filed		
2, 3, 5	as received on	05/07/2001	with letter of 02/07/2001

Claims, No.:

1-8	as received on	05/07/2001	with letter of 02/07/2001
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Drawings, sheets:

1/2, 2/2	as originally filed
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2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/02387

- ☐ the description, pages:
☒ the claims, Nos.:
☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-8
	No: Claims
Inventive step (IS)	Yes: Claims 1-8
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-8
	No: Claims

2. Citations and explanations
see separate sheet

INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET

International application No. PCT/GB00/02387

Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following document: D1 EP-A-0884271

Article 33(2) and (3) PCT

None of the cited prior art documents discloses all the features of the independent claims 1 and 2. Claims 1-8 are therefore novel and fulfill the requirements of Article 33(2) PCT.

D1 is concerned with a methanol reformer which contains a catalyst and is used to supply H_2 to a fuel cell (e.g. claim 1 of D1 and abstract). D1 discusses various ways to reactivate the catalyst whilst it is being used which include:

reducing the fuel load; raising the temperature; increasing the air λ value to increase the O_2 excess

(see col. 3, l. 10-26, claim 1, col. 5, l. 1st paragraph and col. 6, l. 33-36).

For the catalyst to be regenerated the reforming reaction is interrupted according to D1, claim 1. D1 does not specify that fuel, air and steam continue to be passed through a reforming catalyst during the regeneration phase.

In the examples of the application in which fuel, air and steam continue to be passed through a reforming catalyst whilst regeneration occurs, either using air pulses or raised temperature, the Applicant has shown that he can maintain a hydrogen concentration of above 25% throughout the operation (example 2, Fig. 1b, example 3). This effect can also be achieved by increasing the steam feed rate (example 5) or by inhibiting deactivation of the catalyst either using an additive (example 4) or extra air (example 6).

Modulating the fuel feed-rate would also alter the oxygen to carbon ratio and be expected to have a similar effect as modifying the air feed-rate.

Since the methods of claims 1 and 2 are not derivable directly from D1 and the technical effects thereby achieved are not foreseeable from D1 an inventive step is accorded.

Claims 1-8 fulfill the requirements of Article 33(3) PCT.

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Because the performance of the reformer has a direct effect on the power output from the fuel cell, deactivation of the catalyst cannot be allowed to proceed unchecked. However the process of power generation cannot be stopped to allow regeneration of the reformer, when its performance falls below an acceptable level. The regeneration of such catalytic reactors whilst they are in use is the problem this invention sets out to solve.

In many instances, the performance of the catalyst declines while it is being used. Although the rate of decline can usually be reduced by changing the operating conditions, it is often accompanied by a drop in hydrogen and power output. One frequently practised method for restoring the performance of a fuel processor is to replace the catalyst periodically. Another method involves regenerating the catalyst while it remains in the processor, using a prescribed regeneration procedure (eg see JR Rostrop-Nielsen in Catalysis Today, Vol 37, 1997, p 225-232). However, both these require that the process of hydrogen-generation is interrupted in order to restore performance.

Thus in a first aspect, the present invention provides a method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
 - continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
 - continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel,
 - continuing to pass fuel, air and steam through a reforming catalyst wherein an oxygenate additive is added to the feed.
- and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

AMENDED SHEET

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The reforming catalyst may be one component of the catalytic fuel processor, or it may be the only component. Where loss of performance is being caused by a particular component in a complex fuel mixture, the regeneration method can be targeted at the specific deactivating effect.

Thus in a second aspect, the present invention provides a method for preventing or retarding the de-activation of a catalytic fuel processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel,
- continuing to pass fuel, air and steam through a reforming catalyst wherein an oxygenate is added to the feed.

and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

Again, the reforming catalyst may be one component or the only component of the catalytic fuel processor. In a preferred embodiment of the invention water is temporarily added to the feed. ('Feed' is a term used to describe the reactant mixture supplied to the fuel processor.) The water will be rapidly converted into steam in the catalyst. The water (steam) to carbon ratio in the feed may readily be adjusted in order to permit targeting of the regeneration method to a specific deactivating event. Adjusted for the purposes of this invention means increased or decreased. The oxygen to carbon ratio may also be adjusted for the same purpose, by adding or changing the feed-rate of air, or by changing the feed-rate of the fuel.

AMENDED SHEET

PFC1465

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Figure 1b shows the effect of air pulses on the composition of dry reformat during reforming of dodecane (as described in Example 2).

In both cases % in reformat is on the vertical axis and time/hours is on the horizontal axis.

◆ represents Hydrogen, ■ represents carbon dioxide, and ▲ represents carbon monoxide.

Figure 2a shows the composition of dry reformat as a function of time during the reforming of toluene under the two conditions described in example 5.

Figure 2b shows the effect of increasing the air feed-rate on the composition of dry reformat during reforming of toluene (as described in example 6).

In both cases the left hand side of the vertical axis represents % in reformat and the right hand side of the vertical axis represents temperature in °C. The horizontal axis represents time/hours; ◆ represents hydrogen, ■ represents carbon dioxide, ▲ represents carbon monoxide and x represents temperature.

It will be appreciated that many variations can be made to the invention herein described without departing from the present inventive concept.

Example 1 (Aliphatic fuel ; no regeneration)

A bed (0.2 g) of reforming catalyst was packed into a tubular quartz reactor, which was positioned at the centre of a furnace. A mixture of dodecane vapour (produced by vaporising the liquid at a rate of $4 \text{ cm}^3 \text{ hour}^{-1}$), air ($200 \text{ cm}^3 \text{ min}^{-1}$) and steam (produced by vaporising water at a rate of $4 \text{ cm}^3 \text{ hour}^{-1}$) was passed through the catalyst bed, which was heated by the furnace. The furnace temperature was maintained at 500°C . The product stream (ie the reformat) passed through a drier before entering a gas chromatograph, which was used to analyse for hydrogen. The initial concentration of hydrogen in the dry reformat was just above 25%, but declined to 20% within an hour, and to 15% within 4 hours. See Figure 1a for results.

AMENDED SHEET

EPC1465

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CLAIMS

1. A method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,

- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,

- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.

- continuing to pass fuel, air and steam through a reforming catalyst wherein an oxygenate is added to the feed.

and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

2. A method for preventing or retarding the de-activation of a catalytic fuel processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,

- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,

- continuing to pass air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.

- continuing to pass fuel, air and steam through a reforming catalyst wherein an oxygenate is added to the feed.

AMENDED SHEET

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and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

3. A method according to either claim 1 or claim 2, whereby water is temporarily added to the fuel.

4. A method according to claims 1 or 2 in which air is temporarily added to the feed.

5. A method according to claims 1 or 2 in which an oxygenate is added to the feed.

6. A method according to claim 5 in which the oxygenate is MTBE (methyl-tert-butylether).

7. A method according to claims 1 or 2 in which the catalyst bed temperature is raised temporarily by an external heat source.

8. A method according to claims 1 or 2 in which the temperature of one or more of the reactant feeds is raised temporarily.

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(54) Title: PROCESS FOR THE REGENERATION OF REFORMING CATALYSTS

(57) Abstract: The present invention relates to methods for the regeneration of catalytic reactors. In particular it relates to methods for regenerating a fuel-processing catalyst whilst it is still being used to supply hydrogen to a fuel cell. The temperature of the catalyst may be adjusted, the air, steam or fuel feed rate may be adjusted. Alternatively, additives may be added to the feed.

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PROCESS FOR THE REGENERATION OF REFORMING CATALYSTS

The present invention relates to methods for the regeneration of catalytic reactors.

5

Catalytic converters are frequently used in internal combustion engines in order to meet the various regulations concerning the levels of pollutants in exhaust gases. A three-way catalyst is a common form of converter used. This has three main duties, namely, the oxidation of CO, the oxidation of unburnt hydrocarbons (HC's) and the
10 reduction of NOx to N₂. Such catalysts require careful engine management to ensure that the engine operates at or close to stoichiometric conditions, that is fuel/air $\lambda=1$. Growing awareness of the need to conserve the earth's resources and increasingly stringent legislation have recently prompted a search for cleaner and more efficient alternatives to the internal combustion engine. One of the most promising of these is the
15 combination of an electric motor and a fuel cell. However, the latter requires a source of hydrogen, for which there is no supply and distribution infrastructure comparable to that for liquid fuels.

The use of fuel cells is not just limited to vehicle applications. Emergent markets
20 include domestic co-generation of heat and power, and power generation in remote locations. Again, the availability of hydrogen is a key issue, with natural gas often being the preferred fuel for domestic systems, and liquid hydrocarbons being more transportable to remote locations.

25 The problems of hydrogen supply and distribution can be overcome by generating it within the fuel-cell system. A hydrogen-rich gas stream, commonly known as 'reformat', can be produced by catalytically converting organic fuels (such as gasoline, natural gas or alcohol). The process, which is referred to as 'reforming' or 'fuel-processing', can occur by a number of different reaction mechanisms :

- 30
- dissociation (splitting of the fuel molecules),
 - steam reforming (reaction of the fuel with H₂O),
 - partial oxidation (reaction of the fuel with O₂, usually supplied as air)
 - combinations of the above reactions.

Because the performance of the reformer has a direct effect on the power output from the fuel cell, deactivation of the catalyst cannot be allowed to proceed unchecked. However the process of power generation cannot be stopped to allow regeneration of the reformer, when its performance falls below an acceptable level. The regeneration of such catalytic reactors whilst they are in use is the problem this invention sets out to solve.

In many instances, the performance of the catalyst declines while it is being used. Although the rate of decline can usually be reduced by changing the operating conditions, it is often accompanied by a drop in hydrogen and power output. One frequently practised method for restoring the performance of a fuel processor is to replace the catalyst periodically. Another method involves regenerating the catalyst while it remains in the processor, using a prescribed regeneration procedure (eg see JR Rostrup-Nielsen in Catalysis Today, Vol 37, 1997, p 225-232). However, both these require that the process of hydrogen-generation is interrupted in order to restore performance.

Thus in a first aspect, the present invention provides a method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

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- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

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and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

The reforming catalyst may be one component of the catalytic fuel processor, or it may be the only component. Where loss of performance is being caused by a particular component in a complex fuel mixture, the regeneration method can be targeted at the specific deactivating effect.

5

Thus in a second aspect, the present invention provides a method for preventing or retarding the de-activation of a catalytic fuel processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

- 10 - continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
 - continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
 - 15 - continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel,
 - continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.
- 20 and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

Again, the reforming catalyst may be one component or the only component of the catalytic fuel processor. In a preferred embodiment of the invention water is temporarily added to the feed. ('Feed' is a term used to describe the reactant mixture supplied to the fuel processor.) The water will be rapidly converted into steam in the catalyst. The water (steam) to carbon ratio in the feed may readily be adjusted in order to permit targeting of the regeneration method to a specific deactivating event. Adjusted for the purposes of this invention means increased or decreased. The oxygen to carbon ratio may also be adjusted for the same purpose, by adding or changing the feed-rate of air, or by changing the feed-rate of the fuel.

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The catalyst may contain one or more base metals, which may include copper (often used for reforming methanol) and nickel (used for reforming natural gas and higher hydrocarbons). Alternatively, the catalyst may contain one or more precious metals, which may include gold, platinum, palladium, iridium, silver, rhodium and ruthenium. Furthermore, it may contain both base metal(s) and precious metal(s). The catalyst may also contain refractory materials, such as ceramics, metal oxides, perovskites, metal carbides and metal sulphides.

Additives may be added to the feed for various purposes, including acceleration of start-up of a fuel-processor, and the prevention or inhibition of its deactivation. Alternatively, a fuel to which additives have been added during manufacture can be used. In a preferred embodiment of the invention, the additive is an oxygenate, and in an especially preferred embodiment the oxygenate is MTBE (methyl-tert-butylether).

In order to facilitate the regeneration procedure, the temperature of the catalyst bed may be raised temporarily by an external energy source. Within a fuel cell system, the external energy source may be an electrical heater, or a burner (which combusts either some of the fuel or some of the hydrogen produced). In addition, or alternatively, the temperature of one or more of the feed components may be raised temporarily, again by an external heat source.

Among the most common causes of deactivation of a fuel-processor is the retention of carbon or sulphur species by the catalyst. Therefore, in a further embodiment of the invention, catalyst regeneration may occur by removal of the carbon or sulphur species. The carbon species originate from the fuel molecules, and indicate the occurrence of undesired side reactions. The sulphur species originate either from indigenous contaminants in the fuel or from compounds deliberately added to the fuel (such as the odourants used to give natural gas its recognisable smell).

The present invention will now be described by way of the following examples in which:

Figure 1a: shows the composition of dry reformat as a function of time during reforming of dodecane (under conditions described in Example 1).

Figure 1b shows the effect of air pulses on the composition of dry reformat during reforming of dodecane (as described in Example 2).

In both cases % in reformat is on the vertical axis and time/hours is on the horizontal axis.

- 5 ◆ represents Hydrogen, ■ represents carbon monoxide, and ▲ represents carbon monoxide.

Figure 2a shows the composition of dry reformat as a function of time during the reforming of toluene under the two conditions described in example 5.

- 10 Figure 2b shows the effect of increasing the air feed-rate on the composition of dry reformat, during reforming of toluene (as described in example 6).

In both cases the left hand side of the vertical axis represents % in reformat and the right hand side of the vertical axis represents temperature in °C. The horizontal axis represents time/hours; ◆ represents hydrogen, ■ represents carbon dioxide,

- 15 ▲ represents carbon monoxide and x represents temperature.

It will be appreciated that many variations can be made to the invention herein described without departing from the present inventive concept.

20 **Example 1 (Aliphatic fuel ; no regeneration)**

- A bed (0.2 g) of reforming catalyst was packed into a tubular quartz reactor, which was positioned at the centre of a furnace. A mixture of dodecane vapour (produced by vaporising the liquid at a rate of 4 cm³ hour⁻¹), air (200 cm³ min⁻¹) and
25 steam (produced by vaporising water at a rate of 4 cm³ hour⁻¹) was passed through the catalyst bed, which was heated by the furnace. The furnace temperature was maintained at 500°C. The product stream (ie the reformat) passed through a drier before entering a gas chromatograph, which was used to analyse for hydrogen. The initial concentration of hydrogen in the dry reformat was just above 25%, but declined to 20% within an
30 hour, and to 15% within 4 hours. See Figure 1a for results.

Example 2 (Regeneration by air pulses)

The test procedure described in Example 1 was repeated with a fresh charge of catalyst, except that every 10 minutes the air feed-rate was increased to 350 cm³ min⁻¹ for 30 seconds. Apart from the duration of the extra air pulses, the concentration of hydrogen in the dry reformat remained above 25% during 3 hours of testing. See Figure 1b for results.

Example 3 (Regeneration by temperature excursions)

The test procedure described in Example 1 was repeated with a fresh charge of catalyst. Whenever the hydrogen concentration in the dry reformat dropped below 25%, it could be restored by raising the furnace temperature to 600°C for 1 minute.

Example 4 (Inhibition of de-activation by MTBE addition)

The test procedure described in Example 1 was repeated with a fresh charge of catalyst, except that 10% (by volume) methyl-tert-butylether was added to the dodecane. The hydrogen concentration in the dry reformat remained above 25% throughout 5 hours of testing.

Example 5 (Aromatic fuel ; no regeneration)

A bed (0.2 g) of reforming catalyst was packed into a tubular quartz reactor, which was positioned at the centre of a furnace. A mixture of toluene vapour (produced by vaporising the liquid at a rate of 4 cm³ hour⁻¹), air (175 cm³ min⁻¹) and steam (produced by vaporising water at a rate of 4 cm³ hour⁻¹) was passed through the catalyst bed, which was heated by the furnace. The furnace temperature was maintained at 500°C. The initial concentration of hydrogen in the dry reformat was 33%, but declined to 25% within 3 hours. When the catalyst was replaced by a fresh charge and the feed-rate of steam was doubled (by increasing the rate of vaporising water to 8 cm³

hour⁻¹), the initial concentration of hydrogen in the dry reformat was 37%. Within 3 hours, the hydrogen concentration had declined to 30%. See Figure 2a for results.

Example 6 (Prevention of de-activation by extra air)

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The test procedure described in Example 5 was repeated with a fresh charge of catalyst, except that the air feed-rate was increased to 200 cm³ min⁻¹. The initial concentration of hydrogen in the dry reformat was 32%. The concentration remained unchanged during 3 hours of testing. See Figure 2b for results.

10

CLAIMS

1. A method for regenerating a catalytic fuel processor, while it is being used to supply hydrogen to a fuel cell, comprising any one or more of the steps of:

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- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass, air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

15

and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

2. A method for preventing or retarding the de-activation of a catalytic fuel processor while it is being used to supply hydrogen to a fuel cell comprising any one or more of the steps of:

20

- continuing to pass fuel, air and steam through a reforming catalyst whilst the catalyst is heated by an external heat source such that the temperature of the catalyst may be adjusted,
- continuing to pass fuel, air and steam through a reforming catalyst and modulating the air and/or steam feed rate,
- continuing to pass air, fuel and steam through a reforming catalyst and modulating the feed-rate of the fuel.
- continuing to pass fuel, air and steam through a reforming catalyst wherein additive is added to the feed.

25

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and maintaining the hydrogen concentration in dry reformat above 25% throughout the operation of the processor.

3. A method according to either claim 1 or claim 2, whereby water is temporarily
5 added to the fuel.

4. A method according to claims 1 or 2 in which air is temporarily added to the feed.

10 5. A method according to claims 1 or 2 in which an additive is added to the feed.

6. A method according to claim 5 in which the additive is an oxygenate.

7. A method according to claim 6 in which the oxygenate is MTBE
15 (methyl-tert-butylether).

8. A method according to claims 1 or 2 in which the catalyst bed temperature is raised temporarily by an external heat source.

20 9. A method according to claims 1 or 2 in which the temperature of one or more of the reactant feeds is raised temporarily.

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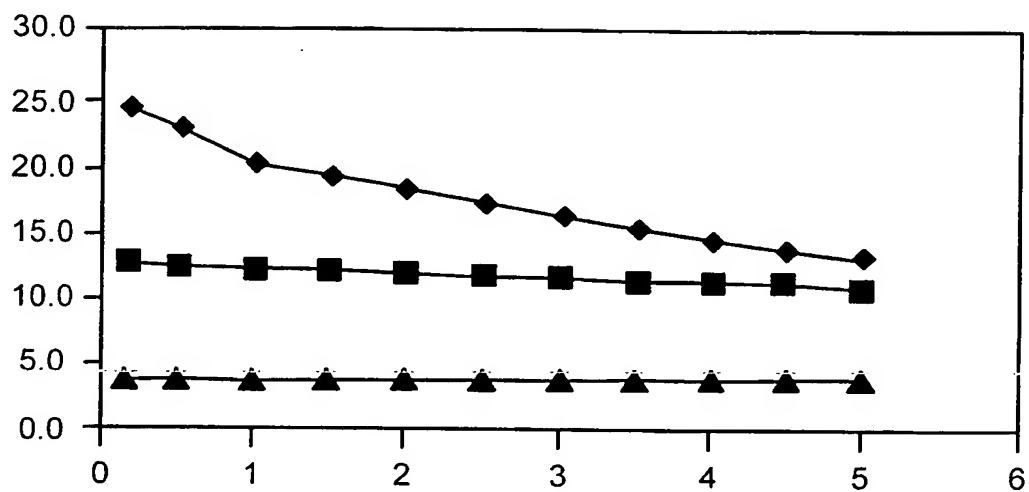


FIG. 1a

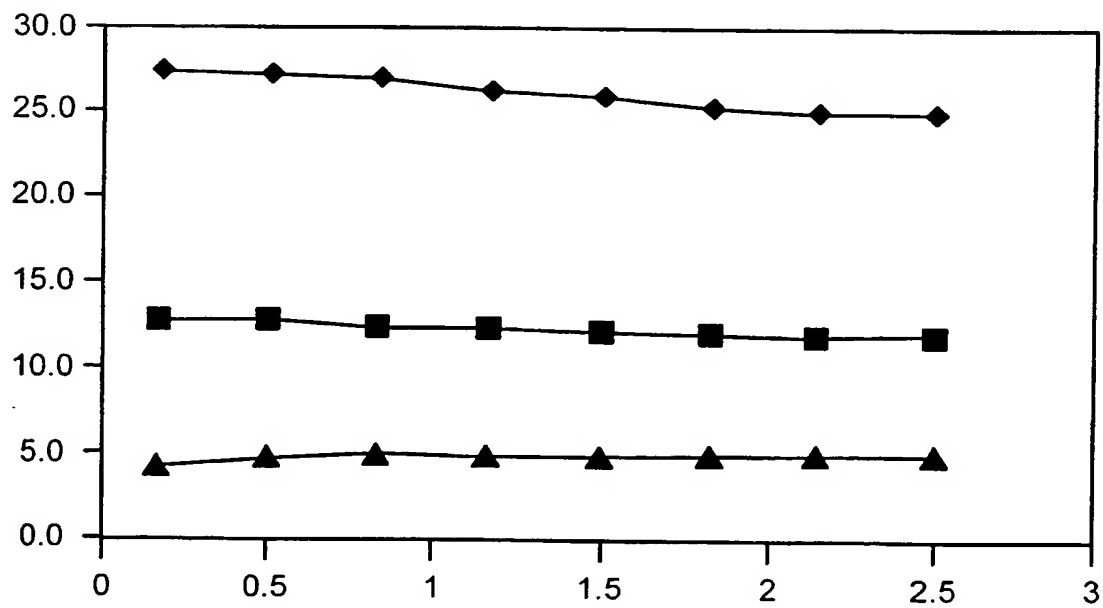


FIG. 1b

2 / 2

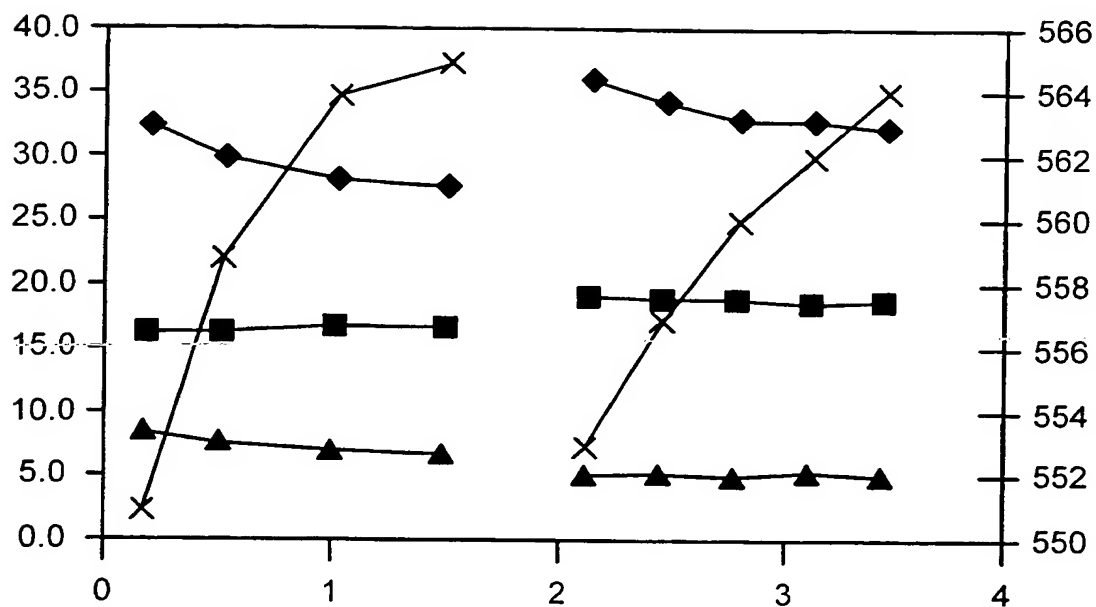


FIG. 2a

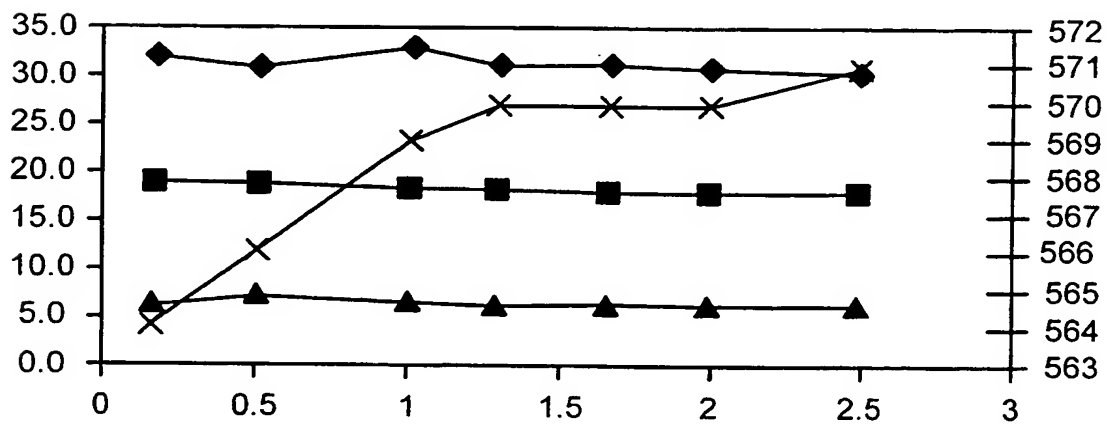


FIG. 2b

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B3/40 C01B3/32 B01J38/06 B01J38/04

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Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data, PAJ, INSPEC, COMPENDEX, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 884 271 A (DBB FUEL CELL ENGINES GMBH) 16 December 1998 (1998-12-16) the whole document	1,2,5,8, 9
A	US 4 089 941 A (VILLEMIN BERNARD) 16 May 1978 (1978-05-16) claim 7	1,2
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A	US 4 083 799 A (ESTES JOHN HAROLD ET AL) 11 April 1978 (1978-04-11) column 6, line 14 - line 18	1,2
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

Date of the actual completion of the international search

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A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 079702 A (TOYOTA CENTRAL RES & DEV LAB INC), 23 March 1999 (1999-03-23) abstract	1,2,4
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International Application No

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